Mounting Powder Samples for Sub-Kelvin Neutron Diffraction

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The increasing availability of commercial ^{3}He cooling systems is making sub-Kelvin temperatures accessible to a much broader community. Unfortunately, the move from pumped ^{4}He-based cryostats (T_{min} ~ 1.5 K) to ^{3}He-based systems (T_{min} < 0.3 K) brings with it severe sample equilibration problems that may not be widely appreciated. Cooling the thermometers that are bolted to the ^{3}He pot and to the end of an oxygen-free highconductivity (OFHC) copper sample holder is relatively straightforward, however, a powdered sample contained within the holder may exhibit cooling times of days.

Our direct experience with equilibration problems while working on $Er_3Cu_4X_4$ (X = Si, Ge, Sn) [1] and an iron-based molecular magnet [2] led us to investigate mounting strategies for powder samples.

Conventional ^{4}He exchange-gas coupling between the sample and the cryostat cold stage, common at higher temperatures, cannot be used in ^{3}He cryogenic systems because the saturated vapour pressure of ^{4}He drops very rapidly at low temperatures making it ineffective as an exchange gas. In addition, limitations on both the cooling power and the total cooling capacity available with sorb-pumped ^{3}He cryogenic systems make it critically important to thermally isolate the ^{3}He stage and its associated sample mount from the surroundings. This requirement leads to cryostat designs in which the sample holder is either bolted directly onto the ^{3}He pot or onto an OFHC copper extension rod that is in turn bolted to the ^{3}He pot. The sample holder and ^{3}He pot are then surrounded by radiation shields and enclosed in a hard vacuum for thermal isolation. Cooling of the sample relies entirely on thermal conduction through the OFHC copper to the walls of the holder and then to the sample itself.

For insulators or powder samples with large numbers of poor electrical contacts, phonons must provide the thermal transport, and these suffer from two problems at very low temperatures: (i) the number density of phonons falls as T^3, so progressively fewer carries are available for conduction; (ii) acoustic mis-match at the copper-sample interface and also at the sample-sample boundaries in powders reduces the efficiency of phonon transport and leads to a Kapitza resistance, R_K, that grows as ~ T^{-3} [3, 4]. As a result, cooling an insulating or poorly connected powder sample becomes increasingly difficult as the temperature drops and it is very easy to have the sample fall out of equilibrium.

Our simplest and most direct solution to the thermal conduction problem was to mix the powdered sample with an approximately equal volume of copper powder and hydraulically press the mixture into an OFHC copper sample holder to form a solid plug. The temperature dependence of several magnetic reflections shown in Fig. 1 reveals the complexity of the magnetic ordering in $Er_3Cu_4Si_4$. We emphasise that the intensities shown in Fig. 1 were derived from measurements made in an essentially random temperature sequence, both on heating and on cooling, with many points interleaved between others. No time-delay or hysteretic effects were detected, indicating that the sample equilibrated in at most a few tens of minutes. Given the rapid equilibration, and the complexity of the magnetic order in $Er_3Cu_4Si_4$, we adopted this material as a standard for evaluating other mounting methods and regarded the intensity data shown in Fig. 1 as providing an empirical temperature scale.

While the hydraulically packed samples exhibit effectively instant equilibration (for neutron scattering purposes) and so leave no doubt as to the actual measurement temperature, the process is somewhat destructive, and the sample is not readily available for other studies once it has been mounted. We therefore evaluated the effectiveness of small amounts of helium gas sealed in with the sample as an alternative strategy. We built an indium-sealed OFHC copper sample holder and initial test cycling in liquid nitrogen and later tests down to 0.3 K confirmed that the seal was reliable.

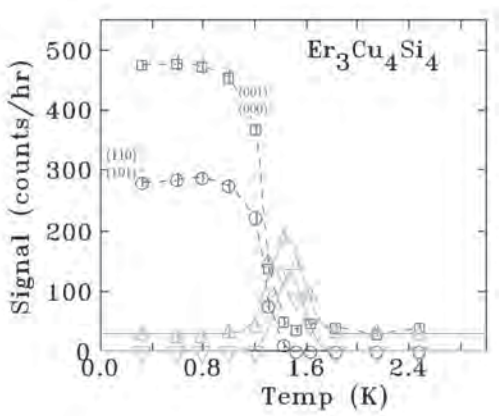

Fig 1. Temperature dependence of several magnetic reflections from Er3Cu4Si4, mixed and pressed with copper powder, showing the complex evolution of magnetic order at low temperatures. The two strongest peaks associated with the ordering at ~ 1.2 K are the (001)–/(000)± at 2θ = 20.2° (□) and the (110)–/(101)+ at 2θ = 21.1° (○) [5]. The two weaker satellites at 2θ = 19.2° (Δ) and 2θ = 21.7° (∇) occur only between 1.6 K and 1.2 K, and were used to follow the early stages of cooling.

Samples were loaded into the holders as loose powders, with no binder or added copper powder. All loading and sealing was carried out at ambient pressure within a helium-filled glove box. For comparison, the same sample was also loaded in air after all helium had been flushed from the holder. At 0.3 K all of the components of air are very low vapour pressure solids and so this arrangement is effectively equivalent to mounting the sample in vacuum. The sample was established at ~ 3 K

for several hours while the ^{3}He system was brought on line, then the system was taken directly down to its base operating temperature of ~ 0.34 K. Neutron diffraction patterns were collected in 6 minute intervals for about 10 hours.

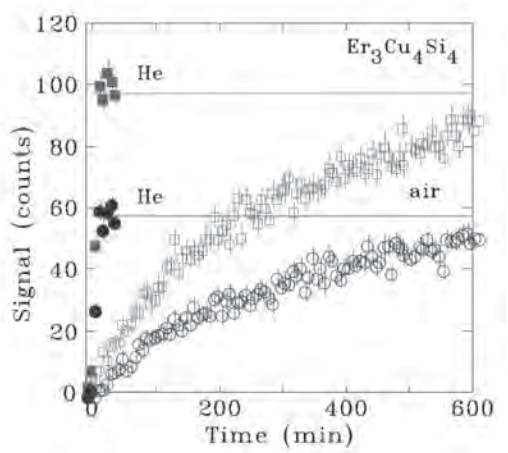

Fig 2. *Time dependence of two magnetic reflections for samples of $Er_3Cu_4Si_4$ sealed under helium (solid symbols) and air (open symbols) showing the very different cooling rates. Symbol shapes correspond to those used in Fig. 1. The solid lines show the expected saturation values for the two peaks at 0.34 K.*

Fig. 2 shows the time dependence of the two magnetic peaks associated with the ordering at 1.2 K in $Er_3Cu_4Si_4$ (see Fig. 1). The differences in cooling behaviour are striking. The two diffraction peaks from the sample loaded under helium reach their saturation intensities by the second measurement (about 12 minutes after the thermometers reached their base temperature) while those from the sample loaded in air are still changing at the end of the run. The sample loaded in air is still cooling 10 hours after the thermometers on the ^{3}He pot and at the end of the sample holder have both reached their final temperatures. It is also clear that the sample loaded in air remains far from ~ 0.34 K after 10 hours of cooling.

A more detailed examination of the diffraction patterns taken with the air-filled sample holder reveals that the two satellite peaks (denoted by Δ and ∇ in Fig. 1) are weaker than the main peaks almost as soon as the thermometers reach their base values. This means that the sample cools through ~ 1.4 K fairly promptly, however this efficient cooling does not continue. After one hour, the sample is at ~ 1.3 K, and the average cooling rate observed through to the end of the experiment was ~ 0.4 mK/minute. The estimated sample temperature after 10 hours was only 1.06(3) K: far hotter than either thermometer and nowhere near the system's base temperature of 0.34 K. A similar failure to cool below 1 K was also observed during initial work on a molecular magnet compound [2] before pressing in copper was adopted.

The substantial difference in cooling rates between in helium and in-air apparent in Fig. 2 serves to emphasise the critical role played by the superfluid ^{4}He film that coats the sample and the interior of the copper sample holder. A sealed vanadium sample holder was tried (superconducting below T_c^V = 5.38 K, so the walls should be thermally insulating) and we found that the cooling rate was indistinguishable from that of the helium-filled OFHC copper sample holder, demonstrating that essentially all of the heat transport is by the superfluid ^{4}He film. We have subsequently built a sealed 7075 aluminium alloy holder that gives weaker Bragg peaks than the copper holder, and a much lower background than the vanadium holder.

We are grateful to the technical staff and instrument scientists of the Canadian Neutron Beam Centre (CNBC) who made these experiments possible. At McGill University: Richard Talbot designed the sealed copper and vanadium sample holders used here, and with Robert Gagnon ensured that they were loaded and sealed properly. Our long-standing collaboration with J.M. Cadogan (U. Manitoba) on the $R_3T_4X_4$ compound family drove the development of the sub-Kelvin sample holders. The $Er_3Cu_4Si_4$ sample used here was prepared by Robert Gagnon (McGill U.).

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